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(Statement A)

# A Renaissance in Noble-Gas Chemistry

Karl O. Christe\*

In spite of the predictions of stable noble-gas compounds since at least 1902, unsuccessful attempts at their synthesis gave rise to the widely held opinion that noble-gases are not only noble but also inert [1]. Thus, dogma-like statements to this effect could be found in practically every chemistry textbook and discouraged for a long time experimentalists to work in this area. It was not until 1962 that this dogma was shattered when Bartlett in Canada [2] and Hoppe in Germany [3] independently discovered with  $\text{XePtF}_6$  and  $\text{XeF}_2$ , respectively, the first stable noble-gas compounds. These discoveries triggered an explosion of worldwide frenzy in this area, and within a short span of time many new xenon, radon and krypton compounds were prepared and characterized. About 30 years and many publications later, new results in this area had slowed down to a trickle, and in the minds of most chemists the chapter on noble-gas chemistry had been completed. A recent burst of startling discoveries, however, shows that noble-gas chemistry is still full of surprises and may signal the beginning of a renaissance in this field.

The recent discoveries fall into four categories: (i), the formation of either new xenon (+II) - hetero-atom linkages or known xenon - hetero-atom connectivities that involve higher oxidation states of xenon; (ii), the ability of  $\text{XeF}_2$  to act as a ligand for numerous naked metal ions; (iii), the

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ability of xenon to act as a complex ligand; and (iv), the observation of the first ground state argon compound containing covalent argon-hetero-atom bonds. In the following paragraphs selected examples are given for recently published or ongoing research in these areas.

In the area of new Xe (+II) - hetero-atom linkages, the first examples of a C-Xe-C group have been prepared independently by two groups. The group of Professor Frohn at the University of Duisburg, Germany, synthesized first  $C_6F_5XeF$  from  $C_6F_5Xe^+$  salts and  $N(CH_3)_4F$  by metathesis and then converted it to  $C_6F_5XeC_6F_5$  and  $C_6F_5XeCN$  by reacting it with  $Cd(C_6F_5)_2$  and  $(CH_3)_3SiCN$ , respectively [4]. In a different approach, the group of Professor Naumann at the University of Koeln, Germany, found that  $C_6F_5XeC_6F_5$  and  $C_6F_5XeF$  are directly accessible from  $XeF_2$  and  $(CH_3)_3SiC_6F_5$  [5]. Furthermore, Frohn and Schroer have recently obtained with  $C_6F_5XeCl$  and  $[C_6F_5XeClXeC_6F_5]^+$  two other interesting new compounds containing both Xe-C and Xe-Cl bonds [6]. These compounds are remarkable because they involve, by analogy with  $XeF_2$ , semi-ionic 3-center/4-electron bonds [7-9] that are only half as strong as the previously known predominantly covalent Xe-C and Xe-Cl bonds in the  $[XeC_6F_5]^+$  [10,11] and  $[XeCl]^+$  [6] cations, respectively. Although the synthesis of  $CF_3XeCF_3$  had been claimed (already) in 1979 [12], all attempts to verify this claim have failed so far [5].

A second example for a novel linkage involving Xe (+II) is the Xe-O-Xe bridge in the  $[FXeOXeFXeF]^+$  cation discovered by Dr. Gerken in Professor Schrobilgen's laboratory at McMaster University [13] in a joint study of the  $XeF^+/H_2O$  reaction system with <sup>the Air Force Research</sup> ~~our~~ laboratory [14].

Another first are novel compounds involving Xe (+IV) - C bonds. From the reaction of  $XeF_4$  with  $C_6F_5BF_2$  the groups of Professors Frohn and Zemva have successfully prepared and characterized the  $C_6F_5XeF_2^+$  cation [15] that was also observed in Prof. Schrobilgen's laboratory in the  $XeF_6/C_6F_5BF_2$  reaction system [16]. Dr. Maggiorosa from Professor Naumann's group has

demonstrated a different approach toward the synthesis of a Xe (+IV) - C bond. By reacting  $\text{XeF}_4$  with the  $\text{CN}^-$  anion he prepared the interesting  $\text{XeF}_4\text{CN}^-$  anion [17]. This anion is noteworthy because it is the (only) third example, besides  $\text{XeF}_5^-$  [18] and  $\text{IF}_5^{2-}$  [19], of a pentagonal planar  $\text{AX}_5$ -type species. Examples for Xe (+VI) - C bonds are still missing. This is not surprising, as the compatibility problems between a strongly oxidizing xenon fragment and a potential fuel ligand increase with an increasing oxidation state and fluorine content of xenon. Two promising approaches to ameliorate this problem involve the synthesis of anions rather than cations, because for a given oxidation state anions are weaker oxidizers than the corresponding cations, and the replacement of fluorine ligand pairs by doubly bonded oxygen atoms. The latter approach has been elegantly demonstrated by Professor Schrobilgen's group for the synthesis of the first examples of the amazing Xe (+VI) - N and Xe (+VIII) - N bonds in the form of  $\text{O}_3\text{Xe-NCCH}_3$ ,  $\text{F}_4\text{OXe-NCCH}_3$ , and  $\text{O}_4\text{Xe-NCCH}_3$ , respectively [20].

In addition to the synthesis and characterization of the above compounds containing novel Xe connectivities, impressive progress was recently made in the characterization of many previously known but poorly characterized noble gas compounds by crystal structure determinations. Typical examples are  $\text{KrF}^+$ ,  $\text{Kr}_2\text{F}_3^+$ ,  $\text{XeNHTeF}_5^+$ ,  $\text{O}_2\text{XeF}^+$ ,  $\text{F}(\text{XeO}_2\text{F})_2^+$ , and  $\text{RCNXeF}^+$  salts by Professor Schrobilgen's group [21] and of  $\text{Xe}_2^+$  by Professor Seppelt's group from the Free University in Berlin [22] that provided an opportunity to obtain an experimental bond length for the only known noble-gas - noble-gas compound. These studies provide much needed structural information, helping us to understand the nature of these compounds.

The second area of interest involves the recent discovery by Professor Zemva's group at the Jozef Stefan Institute in Ljubljana that  $\text{XeF}_2$  can act as a fluorine-bridged ligand for numerous "naked" metal ions [23]. It is based on the reaction of metal  $\text{AsF}_6^-$  salts in anhydrous HF solution with  $\text{XeF}_2$ . If the basicity of  $\text{XeF}_2$  is intermediate between those of HF and the parent metal

fluoride,  $\text{XeF}_2$  can displace HF from the solvation sphere around the metal cation without displacing the metal cation itself under formation of  $\text{Xe}_2\text{F}_3^+$  salts. In this manner,  $[\text{M}(\text{XeF}_2)_m][\text{AsF}_6]_n$  salts have been isolated in which M can be Ag(+1), Ln(+3), Pb(+2), Mg, Ca, Sr, or Ba and m can have values between 2 and 6. A very interesting feature of these salts is the coordination around the metal ions. In the crystal structures determined so far, the metal ions coordinate to fluorine ligands from both  $\text{XeF}_2$  and  $\text{AsF}_6^-$  and exhibit high coordination numbers, typically 8 or 9, resulting in body-centered square antiprisms or trigonal prisms. Clearly, a systematic study of these types of adducts can provide a wealth of information on high-coordination-number chemistry.

The third area of interest is the discovery by Professor Seppelt's group that more than one xenon atom can attach itself to a metal center and form surprisingly stable Au-Xe bonds. Although weakly covalent bonding of a single noble-gas atom to a metal center, such as Cu or Ag in their monohalides or Mn, Fe, Cr, Mo, or W in their pentacarbonyls, had been known, the bonding in  $\text{AuXe}_4^{2+}$  involves 4(!) Xe ligands attached by relatively strong bonds to a single Au (2+) center in a square planar arrangement with a Xe-Au bond length of about 274 pm [24]. This discovery provides not only the first example of xenon acting as multiple ligands but also represents the first strong metal-xenon bond. In view of the generally weak donor abilities of the noble-gases, it remains to be seen if this type of coordination can be extended to other suitable transition metals.

The last subject of this highlight involves the work of Professor Räsänen and his coworkers at the University of Helsinki in Finland. Using low-temperature matrix isolation spectroscopy, they have demonstrated not only the existence of numerous novel xenon- or krypton-hetero-atom bonds, such as Xe-H, Xe-I, Xe-Br, Xe-S, Kr-H, Kr-C, and Kr-Cl, [25] but most significantly have provided experimental evidence for the first predominantly covalent, ground-state argon - hetero-atom bonds, Ar-H and Ar-F in the neutral H-Ar-F molecule [26]. Whereas

weak van der Waals or excited-state argon-hetero-atom bonds had previously been known, vibrationally stable bonds in neutral ground-state argon compounds had been unknown. The H-Ar-F molecule appears to be stable only at very low temperatures in a matrix, and the energy barrier toward the 135 kcal/mol exothermic intramolecular elimination of HF was calculated to be only 8 kcal/mol. As pointed out by Frenking in a recent commentary [27], the H-Ng-F molecules are only kinetically stable, and their stability depends on the energy barriers toward decomposition which can be quite low, particularly in the condensed neat phase. Therefore, HArF is quite different from the many known Xe, Kr and Rn compounds. Also, it should be kept in mind that there are no sharp boundaries between chemical bonds, charge transfer compounds [28], and van der Waals complexes. In HArF, for example, the H-Ar bond has strong covalent contributions, while the Ar-F bond is highly ionic. It is a human trait to put black-and-white labels on an universe consisting mainly of different shades of gray.

Does Räsänen's pioneering work suggest that we can expect to see in the near future the synthesis of marginally stable  $\text{ArH}^+$ ,  $\text{XeH}^+$  or  $\text{ArF}^+$  salts as neat solids? Born-Haber cycle estimates show that solid  $\text{ArH}^+\text{F}^-$  is about 130 kcal/mol endothermic with respect to Ar and HF. Using the very strong Lewis acid  $\text{SbF}_5$  to stabilize the anion as  $\text{SbF}_6^-$ , one can reduce the exothermicity of the decomposition reaction to about 70 kcal/mol. This value implies that a Lewis acid with an  $\text{F}^-$  affinity that exceeds that of  $\text{SbF}_5$  by at least 70 kcal/mol would be required to render this reaction thermally neutral. This is beyond the state of the art in Lewis acid chemistry [29]. The corresponding  $\text{XeH}^+$  salt would be somewhat more favorable, but previous experiments from <sup>The Air Force Research</sup> ~~our~~ laboratory to protonate Xe in HF/ $\text{SbF}_5$  solution at  $-78^\circ\text{C}$  were unsuccessful [30], indicating that a Lewis acid stronger than  $\text{SbF}_5$  is also required in this case. However, the bulk synthesis of marginally stable  $\text{ArF}^+\text{XF}^-$  salts looks more promising, as was also concluded in a previous study [31]. Our Born-Haber cycle estimates indicate that  $\text{ArF}^+\text{SbF}_6^-$  would be unstable by

only 25 kcal/mol relative to Ar, F<sub>2</sub> and SbF<sub>5</sub>, and one can envision Lewis acids of a high enough F<sup>-</sup> affinity to achieve the goal of a marginally stable ArF<sup>+</sup> salt. However, even with a Lewis acid stronger than SbF<sub>5</sub> the synthesis would still present a major challenge because the ArF<sub>2</sub> parent molecule is vibrationally unstable. Therefore, any synthesis of ArF<sup>+</sup> salts will require synthetic methods analogous to those previously used for the syntheses of cations derived from nonexistent parent molecules, such as NF<sub>4</sub><sup>+</sup> [32,33], which involve the use of elemental fluorine in combination with suitable activation energy sources.

This highlight shows that in spite of the relatively small number of laboratories involved in the ongoing efforts, significant breakthroughs have recently been achieved in noble-gas chemistry, heralding a renaissance in this field. In addition to the areas discussed above, one could envision the syntheses of compounds such as XeF<sub>7</sub><sup>+</sup>, XeF<sub>8</sub>, XeOF<sub>5</sub><sup>+</sup>, XeOF<sub>6</sub> or KrF<sub>4</sub>. With today's computational capabilities, the possible existence of these target molecules should be reexamined and, if warranted, experimentally pursued.

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## SYNOPSIS

The synthesis of a vibrationally stable, neutral, and chemically bound ground-state argon compound and recent breakthroughs in xenon chemistry herald a renaissance in noble-gas chemistry.

K. O. Christe\*.....

A Renaissance in

Noble-Gas Chemistry